Complexes of 4,4′-Bipyridine with Some Iron(III) Salts

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Hydrated iron(III) chloride, nitrate, and perchlorate form octahedral co-ordination polymers with 4,4′-bipyridine (4,4′-bipy) in ethanol and methanol media. The iron : 4,4′-bipy ratio is 1 : 1 in all these complexes. In ethanol, $FeCl_3 \cdot 6H_2O$ forms a polymer of empirical formula $Fe(4,4'\text{-bipy})O_{0.5}Cl_2$ containing a linear Fe–O–Fe bridge, while a polymer of empirical formula $Fe(4,4'\text{-bipy})Cl_3$ precipitates from methanol. Hydrated iron(III) nitrate and perchlorate give rise to complexes of empirical formulae $Fe(4,4'\text{-bipy})(NO_3)_3$ and $Fe(4,4'\text{-bipy})(OH_2)_3(ClO_4)_3$, respectively, independent of the solvent (ethanol or methanol) employed in their preparations. Infrared spectra indicate the presence of only bidentate (bridging) 4,4′-bipy in the complexes $Fe(4,4'\text{-bipy})O_{0.5}Cl_2$ and $Fe(4,4'\text{-bipy})Cl_3$. Unidentate (terminal) as well as bidentate (bridging) 4,4′-bipy molecules are present in $Fe(4,4'\text{-bipy})(NO_3)_3$ and $Fe(4,4'\text{-bipy})(OH_2)_3(ClO_4)_3$. Co-ordination of chloride and nitrate is also indicated by the i.r. spectra, while perchlorate is present only as the ionic form.

THE co-ordination chemistry of 4,4′-bipyridine (4,4′-bipy) is in its infancy in comparison to that of its isomer 2,2′-bipy. With Ag^I, Hg^{II}, Co^{II}, Ni^{II}, Cu^{II}, Mn^{II}, and Fe^{II}, 4,4′-bipy yields [1,2] polymeric complexes which are insoluble in water and common organic solvents and which exhibit a metal : 4,4′-bipy ratio of 1 : 1. Complexes with a metal : 4,4′-bipy ratio of 1 : 2 have been prepared for Cu^{II}, Co^{II}, and Ni^{II}.[1] Recently, Anagnostopoulos reported [3,4] water-insoluble 1 : 1 and 1 : 2 complexes, respectively, of 4,4′-bipy with iron(III) chloride and bromide. Here, I present the preparation and characterization of the complexes of 4,4′-bipy with iron(III) chloride, nitrate, and perchlorate in ethanol and methanol media. The observation that $FeCl_3 \cdot 6H_2O$ formed a water-soluble complex with 4,4′-bipy, contrary to the report of Anagnostopoulos,[3] prompted this investigation.

EXPERIMENTAL

Iron(III) chloride hexahydrate (Carlo Erba) and iron(III) nitrate nonahydrate (B.D.H.) were dried *in vacuo* at room temperature to remove any extra moisture and free acid.† Iron(III) perchlorate was prepared by the method of Mulay and Selwood [5] and dried in a vacuum oven at 45 °C to remove excess of perchloric acid. 4,4′-Bipyridine (B.D.H.) was purified by recrystallization from water.

Preparation of Complexes.—The following general procedure was employed in the preparation of all the complexes. 4,4′-Bipyridine (1.0 g, 6.4 mmol) was dissolved in 95% ethanol (*ca.* 50 cm³), except for complex (2), $Fe(4,4'\text{-bipy})Cl_3$ (Table), which was prepared in anhydrous methanol. A solution of the hydrated iron(III) salt (6.4 mmol in *ca.* 50—100 cm³ of the solvent) was added to the 4,4′-bipy solution with stirring.‡ The precipitate, which formed immediately, was collected by filtration, washed with the same solvent used in the preparation, and dried *in vacuo* at room temperature. The elemental analyses results are included in the Table. Complex (2) is brownish yellow while the others are light brown.

Analyses.—Carbon, hydrogen, and nitrogen were determined by the Alfred Bernhardt Microanalyses Laboratory, Germany. Iron was determined spectrophotometrically as $[Fe(phen)_3]^{2+}$ (phen = 1,10-phenanthroline).[6] Chloride was determined by the Volhard method in a strongly acidic medium.[7]

Physical Measurements.—Electronic-absorption spectra were recorded on a Zeiss RPQ-20A recording spectrophotometer, and the reflectance spectra of solid samples were obtained with a Zeiss RA20 reflectance attachment. Infrared spectra in the 650—4 000 cm⁻¹ region were recorded on a Perkin-Elmer 137 spectrometer using Nujol or halogenocarbon oil mulls between potassium bromide plates. In order to avoid the probable replacement of co-ordinated ligands by bromide from the potassium bromide

Analytical, magnetic, and Mössbauer-spectral data

	Analysis (%) [a]					$\mu_{eff.}$ [b]	I.s. [c,d]	Q.s [c]
Complex	C	H	N	Cl	Fe	B.M.	mm s⁻¹	
$Fe(4,4'\text{-bipy})O_{0.5}Cl_2$ (1)	41.3 (41.6)	2.8 (3.0)	9.6 (10.0)	24.4 (24.1)	19.2 (18.8)	2.80	0.39	1.37
$Fe(4,4'\text{-bipy})Cl_3$ (2)	37.7 (38.1)	2.5 (2.7)	8.8 (9.1)	33.4 (33.2)	17.5 (17.3)	5.70	0.35	0.76
$Fe(4,4'\text{-bipy})(NO_3)_3$ (3)	30.2 (30.8)	2.0 (2.2)	7.0 (7.5)		14.0 (13.7)	5.60	0.31	0.73
$Fe(4,4'\text{-bipy})(OH_2)_3(ClO_4)_3$ (4)	21.3 (21.7)	1.4 (1.5)	4.9 (5.2)		9.9 (9.7)	5.30	0.35	0.71

[a] Calculated values are given in parentheses. [b] ±0.20 B.M. at 293 K. [c] ±0.01 mm s⁻¹ at 293 K. [d] Isomer shifts are relative to the centre of the spectrum of a natural iron absorber.

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† Free acid in the iron(III) salts should be avoided since it results in the formation of an alcohol-insoluble white salt with 4,4′-bipy, and precipitates along with the iron(III) complex.

‡ The iron : 4,4′-bipy ratio is 1 : 1 in the precipitate of the complex and is independent of the addition of a one- to three-fold molar excess of iron(III) salt to 4,4′-bipy, or of an iron(III) salt to a one- to three-fold molar excess of 4,4′-bipy.

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plates, the plates were coated with a fine film of polystyrene whose absorptions were cancelled out by placing an identical set of polystyrene-coated plates in the reference beam. A Perkin-Elmer model 180 spectrometer was employed for the 200—650 cm^{-1} region, using Nujol mulls and polyethylene windows. Mössbauer spectra were recorded with a constant-acceleration velocity transducer coupled to a ^{57}Co-in-Cu matrix source in the standard transmission geometry. The velocity calibration was made with metallic iron as a standard. Cylindrical acrylic cells of cross-sectional area 2 cm^2 were used to contain the powdered samples. Liquid samples or solutions in the sample holder were cooled to liquid-nitrogen temperature by dipping directly into liquid nitrogen (cooling rate 450 °C min^{-1}) before introducing into the cell compartment. Magnetic susceptibilities were obtained by use of a Varian A-60 proton n.m.r. spectrometer.[8] Powdered $Cu[SO_4]\cdot 5H_2O$ and aqueous $CuCl_2$ solutions were used as reference standards. Measurements were made at 293 K. Conductivities were measured with a Beckman model RC-16B2 conductivity bridge and a cell with two platinum electrodes. The cell constant was 0.01. The concentration of the solutions was 0.001 mol dm^{-3}.

RESULTS AND DISCUSSION

All the complexes reported in this work have an iron : 4,4'-bipy ratio of 1 : 1 (Table) and, except for (3), they are soluble in water. Complex (3), $Fe(4,4'\text{-bipy})(NO_3)_3$, is soluble in water immediately after its preparation, but noticeably decreases in solubility with ageing. This decrease in solubility may be attributed to an increase in polymerization. Complex (4), $Fe(4,4'\text{-bipy})(OH_2)_3(ClO_4)_3$, is soluble in water as well as methanol.

Iron(III) chloride hexahydrate gave two different complexes depending on the solvent (ethanol or anhydrous methanol) employed in the preparation. Complex (1), $Fe(4,4'\text{-bipy})O_{0.5}Cl_2$, prepared in 95% ethanol, exhibits a strong broad absorption at 850 cm^{-1} in the i.r. spectrum which is absent in the spectrum of complex (2), $Fe(4,4'\text{-bipy})Cl_3$, isolated from anhydrous methanol. Since this absorption is characteristic of a linear Fe–O–Fe asymmetric stretching vibration,[9–11] complex (1) contains Fe–O–Fe bridge bonds. It is known that iron(III) complexes containing linear Fe–O–Fe bridges exhibit a low magnetic moment due to the exchange interactions of the *d* electrons of the two metal ion centres.[9,12–16] Complex (1) exhibits a magnetic moment of 2.80 B.M.* per iron(III) ion, while (2) gives a moment of 5.60 B.M. per iron(III) ion. The value for (2) suggests a high-spin octahedral iron(III) ion, while the low value for (1) may be attributed to the exchange interactions of the *d* electrons of two high-spin octahedral iron(III) centres.

Further evidence for the presence of a linear Fe–O–Fe bridge in (1) is provided by the Mössbauer spectral results. Complex (1) exhibits quadrupole-splitting (q.s.) and isomer-shift (i.s.) values typical of iron(III) complexes containing linear Fe–O–Fe bonds,[17–19] while the values (Table) for (2) are in the range expected for a normal high-spin octahedral iron(III) complex.[19]

The far-i.r. spectra of (2) exhibit two strong absorptions at 278 and 260 cm^{-1} which are absent in the spectrum of 4,4'-bipy. These absorptions arise from the co-ordination of Cl^- to Fe^{III}.[20] The presence of two absorptions may indicate the existence of chloride co-ordination in two different environments. Since it is reasonable to assume that (2) is a co-ordination polymer containing bridging 4,4'-bipy molecules, and bridging and terminal chloride groups, the absorptions at 278 and 260 cm^{-1} may reasonably be assigned to terminal and bridging chlorides, respectively.[20]

In addition to the two absorptions attributable to chloride co-ordination, complex (1) also exhibited four absorptions at 300, 350, 415, and 460 cm^{-1}. Due to the complex polymeric nature of (1) a proper assignment of these absorptions is difficult. Since the major difference between (1) and (2) is the existence of a linear Fe–O–Fe bridge in (1), the four absorptions may be attributed to this Fe–O–Fe bridge. The symmetric stretching and bending vibrations of Fe–O–Fe are expected to occur in this region.[21,22]

Based on the present results, it is reasonable to assume that complex (1) is surrounded octahedrally by two bridging 4,4'-bipy, one bridging O^{2-}, and two bridging and one terminal chloride groups. Complex (2) attains octahedral co-ordination by means of two bridging 4,4'-bipy, and two bridging and two terminal chloride groups.

Iron(III) nitrate and 4,4'-bipy gave the same complex independent of the solvent (ethanol or methanol) employed in its preparation. The i.r. spectrum (NaCl region) of this complex shows two absorptions at 1 200 and 1 236 cm^{-1}, while the spectrum of 4,4'-bipy has a single absorption in this region at 1 200 cm^{-1}. The absorptions in this region are due to the CH in-plane bending modes of hydrogens adjacent to the ligand nitrogens. Co-ordination of the ligand nitrogen to

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* Throughout this paper: 1 B.M. $\approx 9.27 \times 10^{-24}$ A m^2.

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Fe^{III} will undoubtedly influence the CH in-plane bending modes. Now 4,4′-bipy may act as a terminal (metal ion co-ordinated to only one hydrogen) or a bridging ligand (the two nitrogen atoms co-ordinated to two different metal ions). If all the 4,4′-bipy molecules are bridging we may expect a single absorption in the 1 200—1 250 cm^{-1} region, while the existence of 4,4′-bipy in terminal and bridging positions would give rise to two absorptions. Hence, it is concluded that terminal as well as bridging 4,4′-bipy molecules are present in (3).* Similar spectral results have been reported for metal complexes of pyrazine.[23]

The i.r. spectra also show the existence of uni- as well as bi-dentate nitrate groups in complex (3). Strong peaks, which are absent in the spectrum of 4,4′-bipy, were observed at 1 296, 1 315, 1 430, and 1 480 cm^{-1} and weak sharp absorptions at 660, 707, 720, and 750 cm^{-1}. The absorptions at 707, 720, 1 315, and 1 430 cm^{-1} are attributable to unidentate nitrate groups, and those at 660, 750, 1 296, and 1 480 cm^{-1} to bidentate nitrate groups.[24] The magnetic-moment and Mössbauer-spectral data for complex (3) (Table) are typical of a high-spin octahedral iron(III) complex. The results suggest that complex (3) attains octahedral co-ordination by means of bridging and terminal 4,4′-bipy molecules, and by bi- and uni-dentate nitrate groups.

Complex (4), prepared from iron(III) perchlorate and 4,4′-bipy in ethanol medium, showed an empirical formula of $Fe(4,4'\text{-bipy})(OH_2)_3(ClO_4)_3$. The presence of co-ordinated water is clearly shown by the absorptions at 3 500, 1 620, and 815 cm^{-1} in the i.r. spectra. The perchlorate groups are ionic in nature as shown by a strong and broad absorption at 1 000—1 150 cm^{-1} and a very weak absorption at 920 cm^{-1}.[25,26] Two medium-intensity absorptions were observed at 1 200 and 1 230 cm^{-1} showing the presence of bridging as well as terminal 4,4′-bipy molecules. The magnetic-moment and Mössbauer-spectral data (Table) are typical of a high-spin octahedral iron(III) complex. Hence, complex (4) is considered to be an octahedral polymer containing water molecules and bridging as well as terminal 4,4′-bipy in the co-ordination sphere.

The electronic-absorption spectra of aqueous solutions, and reflectance spectra, of (1)—(4) are in agreement with octahedral high-spin iron(III) complexes. All the complexes exhibit charge-transfer absorptions in the 300—500 nm region. The spectra of aqueous solutions are identical and, hence, show the presence of identical absorbing molecules.

Dissolution of (1) in water effects the destruction of the Fe–O–Fe bridge as shown by the Mössbauer-spectral results for a frozen solution (i.s. 0.35 and q.s. 0.57 mm s^{-1}) and magnetic-moment data ($\mu_{eff.}$ 5.80 B.M. per iron). All the four complexes exhibit a molar conductance in aqueous solution in the range 420—460 S cm^2 mol^{-1} indicative of a 3 : 1 electrolyte.[27] However, the fact that these complexes are acids, releasing hydrogen ions in an aqueous medium, makes it difficult to interpret the conductivity results. Nevertheless, cation-exchange studies of aqueous solutions of (1) and (2) indicated that the chloride present is not co-ordinated to Fe^{III} in aqueous media. This suggests that, in an aqueous medium, the Fe^{III} in these complexes attains six-co-ordination by means of water molecules and bridging and terminal 4,4′-bipy molecules.

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* Complex (1) or (2) exhibits a single absorption at 1 221 cm^{-1} and, hence, contains only bridging 4,4′-bipy molecules.

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